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High-yielding synthesis of 1-carboxamido-3,4-dihydronaphthalenes via palladium-catalyzed aminocarbonylation

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ABSTRACT

1-Iodo-3,4-dihydronaphthalene, an iodoalkene substrate obtained from α-tetralon, has been carbonylated in the presence of palladium–phosphine precatalysts. Systematic investigations have revealed that the 1-carboxamido-3,4-dihydronaphthalenes and 1-methoxycarbonyl-3,4-dihydronaphthalene have been formed in exceptionally high isolated yields (up to 96%) in chemospecific reaction. The influence of the amine nucleophile and that of the reaction conditions (carbon monoxide pressure, reaction temperature) on the reactivity of the substrate have been investigated.

1. Introduction

The discovery of the carbonylation of aryl halides in the presence of *O*- and *N*-nucleophiles[1] initiated various synthetic routes for the synthesis of esters and amides. The synthetic potential of this carbonylation reaction was illustrated using several aryl halide models and substrates of practical importance as well.[2–6] The intramolecular alkoxy- and aminocarbonylation resulted in the formation of lactones and lactams, respectively.[7] The palladium-catalyzed alkoxy- and aminocarbonylation of aryl halides proved to be of industrial importance and has been reviewed recently.[8,9]

As synthetic analogues to aryl halides, iodo- and bromo-alkenes of various structures have also been synthesized and widely used as substrates in the synthesis of α,β-unsaturated esters and carboxamides in palladium-catalyzed alkoxy- and aminocarbonylations, respectively.[5,6]

As a part of our continuing research in the carbonylation and coupling reactions of iodoalkenes, the synthesis of various building blocks was carried out. Recently, we turned our attention towards the synthesis of compounds with dihydronaphthalene backbone. The pharmacological importance of these derivatives as key moieties has been shown in the synthesis of benzoquinazoline derivatives,[10] tetrahydrobenzoisoquinolines,[11] azasteroids obtained in Diels–Alder reaction[12] and estrane derivatives in diene additions.[13]

The synthesis of key intermediates, such as 1-amino-2-cyano-3,4-dihydronaphthalene derivatives,[14] 1-amino-2-formyl-3,4-dihydronaphthalene,[15] 1-chloro-2-formyl-3,4-dihydronaphthalene,[16] 3,4-dihydronaphthalene-2-carboxylic acid[17] was reported. 3,4-Dihydronaphthalene derivatives have been used in the synthesis of dibenzonaphthyridines,[18] demethoxydaunomycinones,[19] phenantrenones,[20] chromenones,[21] secopseudopterosin aglycone,[22] optically active anthracyliones.[23] The regioselectivity of nucleophilic additions on dihydronaphthalene has been controlled by the chromium-tricarbonyl moiety coordinated to the aromatic ring.[24] Rhodium nanoparticles served as efficient catalysts in the selective hydrogenation of 2-acetyl-5,8-dimethoxy-3,4-dihydronaphthalene to the corresponding 1,2,3,4-tetrahydronaphthalene, a precursor of antitumour anthracyclinic compounds.[25]

Compounds with 3,4-dihydronaphthalene moiety were used as substrates also in various homogeneous catalytic reactions. 1-Bromo-3,4-dihydronaphthalene and its triflate analogue have been used as substrate in Suzuki-[26] and Negishi-reaction,[27] respectively. 6-Aryl- and 1-aryl-substituted 3,4-dihydronaphthalenes were synthesized in the cross-coupling reaction of the corresponding 6-triflate[28] and 1-bromo-3,4-dihydronaphthalene,[29] respectively. Enantioselective Sharpless-dihydroxylation[30] and Jacobsen-epoxidation[31] of functionalized 3,4-dihydronaphthalenes led to the corresponding 1,2-substituted chiral building blocks.

In the present study, a high-yielding palladium-catalyzed chemospecific synthesis of 2-carboxamido- and 2-methoxycarbonyl-3,4-dihydronaphthalene derivatives is reported.

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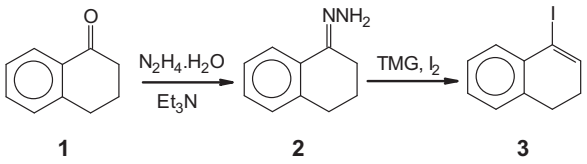
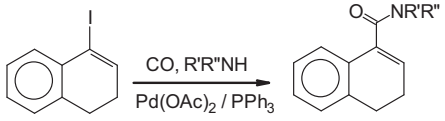
2. Results and discussion

α-Tetralone (**1**) was transformed to the corresponding hydrazone (**2**), which was treated with iodine in the presence of a strong base, TMG (*N*,*N*,*N*′,*N*′-tetramethylguanidine) (Scheme 1). The iodoalkenyl derivative (**3**) was obtained in good yields based on the starting material (**1**). Although a general methodology for preparing iodoalkenes from ketones is known,[32,33] due to the optimization of the procedure a complete description of the preparation of **3** is given in the Section Experimental.



Scheme 1. The synthesis of 1-iodo-3,4-dihydronaphthalene (**3**).

1-Iodo-3,4-dihydronaphthalene (**3**) was aminocarbonylated in the presence of palladium catalysts formed in situ by the reaction of palladium(II) acetate and two molar equiv of triphenylphosphine. *tert*-Butylamine (**a**), aniline (**b**), piperidine (**c**), methyl glycinate (**d**), methyl alaninate (**e**) and methyl prolinate (**f**) were used as *N*-nucleophiles (Scheme 2).



	R′	R″
a	H	*t*Bu
b	H	Ph
c	-(CH$_2$)$_5$-	
d	H	CH$_2$COOCH$_3$
e	H	CH(CH$_3$)COOCH$_3$
f	-CH(COOCH$_3$)(CH$_2$)$_3$-	

Scheme 2. Aminocarbonylation of **3** towards carboxamides (**4**).

It is worth mentioning, that the above Pd(OAc)$_2$/2PR$_3$-type catalyst is widely used as a precursor of 'in situ' formed palladium(0)-tertiary phosphine systems. It has been proved that palladium(II) is reduced to palladium(0) while one of the 2 equiv of phosphine ligands is oxidized.[34–36] In our case, the formation of coordinatively highly unsaturated Pd(PPh$_3$)(S)$_n$ (S stands for solvent (DMF)) complex is supposed while the 'second' equivalent of PPh$_3$ is oxidized to triphenylphosphine oxide. Under the aminocarbonylation conditions used (see below) the action of other compounds (amine, carbon monoxide) as reducing agents cannot be excluded.

A highly chemoselective reaction has been observed in the presence of *tert*-butylamine (**a**) resulting in the formation of the corresponding carboxamide derivative (**4a**). Yields of practical interest were obtained under mild conditions (1 bar CO, 50 °C). Practically complete conversions can be achieved within a few hours reaction time (Table 1, entry 1–5).

The reaction conditions were optimized towards the formation of **4a**. The following effects are worth mentioning: (i) the use of even lower reaction temperature (30 °C) resulted in lower activity (entry 6), (ii) the increase of the carbon monoxide pressure lead to higher conversion, while the high chemoselectivity was still maintained (entry 7–9), (iii) the aminocarbonylation at high carbon monoxide pressure also needs a reaction temperature higher than 30 °C in order to achieve complete conversion (entry 10).

Table 1
Aminocarbonylation of 1-iodo-3,4-dihydronaphthalene (**3**) in the presence of palladium–PPh$_3$ in situ catalysts[a]

Entry	Amine	p (CO) [bar]	R. Time [h]	Conv.[b] [%]	Isolated yield of **4**
1	**a**	1	0.5	75	n.d.
2	**a**	1	1	85	n.d.
3	**a**	1	2	92	n.d.
4	**a**	1	5	96	90 (**4a**)
5	**a**	1	24	>99.8	96 (**4a**)
6[c]	**a**	1	24	78	n.d.
7	**a**	20	5	99	n.d.
8	**a**	40	5	>99.8	95 (**4a**)
9	**a**	60	5	>99.8	96 (**4a**)
10[c]	**a**	60	5	89	n.d.
11	**b**[d]	1	1	72	n.d.
12	**b**[d]	1	24	>99.8	86 (**4b**)
13	**b**[d]	40	5	99	82 (**4b**)
14	**c**[e]	1	1	80	n.d.
15	**c**[e]	1	24	>99.8	90 (**4c**)
16	**c**[e]	40	5	99	n.d.
17	**d**[f]	1	1	85	n.d.
18	**d**[f]	1	24	>99.8	91 (**4d**)
19	**d**[f]	40	5	99	88 (**4d**)
20	**e**[f]	1	1	81	n.d.
21	**e**[f]	1	24	>99.8	92 (**4e**)
22	**e**[f]	40	4	98	85 (**4e**)
23	**f**[f]	1	1	70	n.d.
24	**f**[f]	1	24	>99.8	88 (**4f**)
25	**f**[f]	40	5	98	n.d.

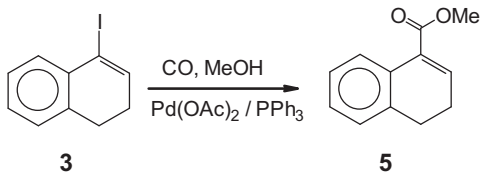
[a] Reaction conditions (unless otherwise stated): 1 mmol of substrate (**1**); 0.025 mmol of Pd(OAc)$_2$; 0.05 mmol of PPh$_3$; 3 mmol of **a**; 0.5 mL of triethylamine; solvent: 10 mL of DMF, reaction temperature: 50 °C; n.d.: not determined.
[b] Determined by GC and GC–MS (naphthalene as internal standard).
[c] Reaction temperature: 30 °C.
[d] 1.5 mmol of **b**.
[e] 2.0 mmol of **c**.
[f] 1.1 mmol of **d**, **e** or **f**. (as a hydrochloride salt).

Screening the various amines in aminocarbonylation, efficient synthesis of the corresponding carboxamides (**4b**–**f**) was carried out. In longer reaction times (24 h) practically complete conversion was achieved in all cases (entries 12, 15, 18, 21 and 24). However, decreasing the reaction time some differences in the reactivities can be observed: (i) the aromatic primary amine (**b**) (entry 11) and the more hindered amino acid-derived secondary amine (**f**) (entry 23) show slightly lower reactivity in aminocarbonylation than the secondary amine (**c**) (entry 14) and the amino acid-derived primary amines (**d** and **e**) (entry 17 and 20), (ii) the increase of the carbon monoxide pressure lead to complete conversion in case of all amines (**b**–**f**) in reasonable reaction times (entries 13, 16, 19, 22 and 25).

In addition to the *N*-nucleophiles specified above methanol as *O*-nucleophile was also investigated. **3** as a substrate was methoxycarbonylated in the presence of 'in situ' formed palladium(0) catalysts. Mild reaction conditions (50 bar CO, 50 °C) and 2.5% palladium catalyst precursor were used. The exclusive formation of the corresponding methyl ester (**5**) was observed and isolated in good yields (up to 78%) (Scheme 3).

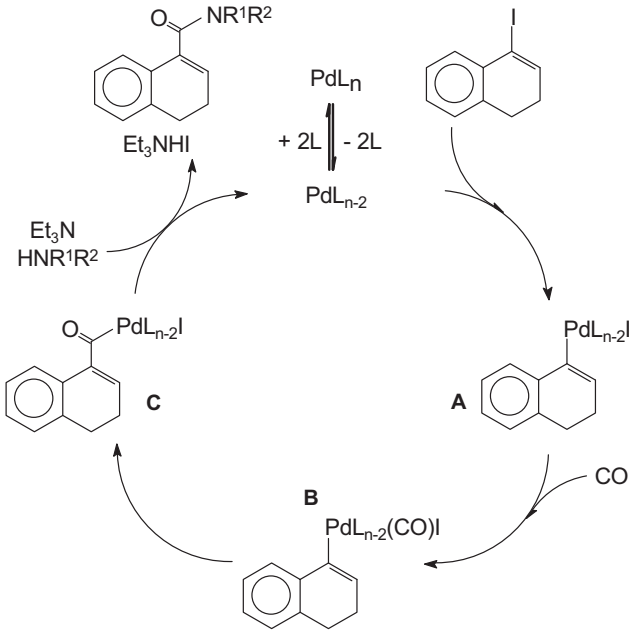
For comparison, the reactivity of structurally analogous compounds, such as α-iodo-styrene[37,38] and α-iodoethenyl-naphthalene isomers[39] was related to that of **3** in carbonylation reactions. It can be stated that the reactivity of the cyclic iodoalkene compound **3** proved to be definitely higher than that of the aforementioned open chain 1-iodo-1-arylalkene type iodoalkenes both in amino- and alkoxycarbonylation reactions.

The increased reactivity of the substrate (**3**) could be explained by the sterically less congested arrangement of the alkenyl-group,



Scheme 3. Methoxycarbonylation of **3** in the presence of palladium catalysts.

and consequently, its facile oxidative addition to palladium(0) resulting in the palladium(II)-alkenyl intermediate (**A**) (Scheme 4). Furthermore, the iodo–carbon bond of **3** has higher polarizability than the corresponding C(sp^2)–X bonds in its structural analogues, such as chloro- and bromo-alkenes. (In general, in line with the decreasing carbon–halide bond energy, the rate of the oxidative addition to palladium(0), and consequently, the efficiency of carbonylations decrease in the order C–I>C(OTf)≥C–Br≫C–Cl ≫C–F.[2,9]) The formation of the terminal carbonyl complex (**B**) is followed by carbon monoxide insertion. The highly reactive acyl intermediate (**C**) gives the amide in the product forming step while the coordinatively unsaturated intermediate is formed.



Scheme 4. The simplified catalytic cycle of the aminocarbonylation of **3**.

3. Conclusions

The aminocarbonylation of 1-iodo-3,4-dihydronaphthalene provides an easy access to 1-carboxamido-3,4-dihydronaphthalenes, the regioisomers of 2-substituted 3,4-dihydronaphthalenes (e.g., 2-carbonitrile/2-carboxaldehyde/2-carboxylic acid-3,4-dihydronaphthalene) with wide pharmacological interest. The above methodology resulted in the highly selective formation of dihydronaphthalene-based α,β-unsaturated amides and esters. All products were isolated in yields of synthetic interest.

4. Experimental

4.1. General procedures

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Inova 400 spectrometer at 400.13 MHz and 100.62 MHz, respectively. Chemical shifts δ are reported in parts per million relative to $CHCl_3$ (7.26 and 77.00 ppm for ^{1}H and ^{13}C, respectively). Elemental analyses were measured on a 1108 Carlo Erba apparatus. Samples of the catalytic reactions were analyzed with a Hewlett Packard 5830A gas chromatograph fitted with a capillary column coated with OV-1 (internal standard: naphthalene; injector temp 250 °C; oven: starting temp 50 °C (hold-time 11 min), heating rate 15 °C min^{-1}, final temp 320 °C; detector temp 280 °C; carrier gas: helium (rate: 1 mL min^{-1})). The FT-IR spectra were taken in KBr pellets using an IMPACT 400 spectrometer (Nicolet) applying a DTGS detector in the region of 400–4000 cm^{-1}, the resolution was 4 cm^{-1}. The amount of the samples was ca. 0.5 mg.

The substrate (**3**) was synthesized by the modified Barton-procedure (See Section 4.2).[32,33] The amine nucleophiles were purchased from Sigma–Aldrich and were used without further purification. It is worth noting that all carboxamides (**4a**–**f**) and the ester (**5**) can be isolated in nearly quantitative yields (up to 96%) being the only products under mild reaction conditions.

4.2. Synthesis of 1-iodo-3,4-dihydronaphthalene (3)

α-Tetralone (**1**) (29.2 g, 0.2 mol), freshly distilled hydrazine hydrate (98%, 60 g, 1.2 mol) and triethylamine (50 g, 0.49 mol) were heated in refluxing methanol (150 mL) for 2.5 h. After completion of the reaction the mixture was poured onto water and extracted with hexane (2×120 mL). Then the combined organic phase was washed with brine (3×70 mL) and water (70 mL), and dried over molecular sieve. After the evaporation of the solvent the crude hydrazone derivative (**2**) was obtained and used in the next step without further purification.

To a stirred solution of iodine (22.6 g, 0.089 mol) in ether (100 mL) *N*,*N*,*N*′,*N*′-tetramethylguanidine (46.3 g, 0.4 mol) was added at ice-bath cooling. To this solution the ethereal solution (30 mL) of **2** (5 g, 0.031 mol) was added dropwise at room temperature. The reaction mixture was stirred for 0.5 h and the precipitated salt was filtered. The solvent was evaporated and the residue was heated at 90 °C under argon atmosphere for 2 h. The mixture was poured onto iced water (250 mL) and extracted with hexane (3×100 mL). The combined organic layer was washed with 1 N aqueous hydrochloric acid (3×50 mL), water (2×50 mL), 5% aqueous sodium hydrogen carbonate (2×50 mL), then with water (2×50 mL), saturated aqueous sodium thiosulfate (3×5 mL) and water (3×5 mL) again. The hexane solution was dried on molecular sieve overnight. The hexane was distilled off and the crude product was distilled under vacuum. The highly pure product (**3**) was used in further experiments as obtained. Yield: 21.5 g; 42% (based on **1**). (In order to avoid its oxidative and photochemical decomposition, **3** has to be kept under argon in refrigerator. By using it in carbonylation reactions, reproducible results can be obtained even after two months. No changes in its colour and analytical characteristics were observed within this time interval.)

4.3. Aminocarbonylation of 1-iodo-3,4-dihydronaphthalene (3) in the presence *N*-nucleophiles under high carbon monoxide pressure

In a typical experiment $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), triphenylphosphine (13.2 mg, 0.05 mmol), 1-iodo-3,4-dihydronaphthalene (256 mg, 1 mmol), amine nucleophile (3 mmol of **a**/1.5 mmol of **b**/2 mmol of **c**/1.1 mmol of **d**, **e** or **f**) and triethylamine (0.5 mL) were dissolved in DMF (10 mL) under argon in a 100 mL autoclave. The atmosphere was changed to carbon monoxide and the autoclave was pressurized to the given pressure by carbon monoxide. The reaction was conducted for the given reaction time upon stirring at 50 °C (or 30 °C) and analyzed by GC–MS. The mixture was then concentrated and evaporated to dryness. The residue was dissolved in chloroform (20 mL) and washed with water (3×20 mL). The organic phase was dried over Na_2SO_4, filtered and evaporated to a crystalline material or to a waxy residue. All compounds were subjected to column chromatography (Silicagel 60 (Merck), 0.063–0.200 mm), EtOAc/$CHCl_3$

(the exact ratios are specified in Section Characterization (4.6) for each compound).

4.4. Aminocarbonylation of 1-iodo-3,4-dihydronaphthalene (3) in the presence *N*-nucleophiles under atmospheric carbon monoxide pressure

In a typical experiment $Pd(OAc)_2$, triphenylphosphine, 1-iodo-3,4-dihydronaphthalene, amine nucleophile and triethylamine were dissolved in DMF (for the quantity of the reagents See Section 4.3) under argon in a 100 mL three-necked flask equipped with a gas inlet, reflux condenser with a balloon (filled with argon) at the top. The atmosphere was changed to carbon monoxide. The reaction was conducted for the given reaction time upon stirring at 50 °C and analyzed by GC–MS (internal standard: naphthalene). The mixture was then concentrated and evaporated to dryness and worked-up as described in Section 4.3.

4.5. Methoxycarbonylation of 1-iodo-3,4-dihydronaphthalene

In a typical experiment $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), triphenylphosphine (13.2 mg, 0.05 mmol), 1-iodo-3,4-dihydronaphthalene (256 mg, 1 mmol), methanol (0.202 mL, 5 mmol) and triethylamine (0.5 mL) were dissolved in DMF (10 mL) under argon in a 100 mL three-necked flask equipped with a gas inlet, reflux condenser with a balloon (filled with argon) at the top. The atmosphere was changed to carbon monoxide. The reaction was conducted for 24 h upon stirring at 50 °C and analyzed by GC–MS (internal standard: naphthalene). The mixture was then concentrated and evaporated to dryness and worked-up as described in Section 4.3.

4.6. Characterization of the products

*4.6.1. 1-Iodo-3,4-dihydronaphthalene (**3**).* Yield: 21.5 mg (42%); highly viscous yellow material; [found: C, 46.65; H, 3.61; $C_{10}H_9I$ requires C, 46.90; H, 3.54%]; R_f (10% EtOAc/$CHCl_3$) 0.90; δ_H (400 MHz, $CDCl_3$) 7.45 (1H, d, 7.6 Hz, Ar–H), 7.2 (1H, t, 7.4 Hz, Ar–H), 7.15 (1H, t, 7.5 Hz, Ar–H), 7.0 (1H, d, 7.2 Hz, Ar–H), 6.8 (1H, t, 4.8 Hz, =CH), 2.85 (2H, t, 7.9 Hz, CH_2), 2.4 (2H, m, =CHCH_2). δ_C (100.6 MHz, $CDCl_3$) 140.0, 135.8, 134.3, 130.8, 128.2, 127.2, 126.9, 98.0, 27.8, 27.1; IR (KBr ν (cm^{-1})): 1604 (C=C); MS *m*/*z* (rel int.): 256 (63, M^+), 128 (100), 102 (11).

*4.6.2. 1-(N-tert-Butylcarboxamido)-3,4-dihydronaphthalene (**4a**).* Yield: 220 mg (96%); off-white solid, mp 94–95 °C; [found: C, 78.41; H, 8.51; N, 8.20; $C_{15}H_{19}NO$ requires C, 78.56; H, 8.35%]; R_f (10% EtOAc/$CHCl_3$) 0.82; δ_H (400 MHz, $CDCl_3$) 7.41 (1H, d, 7.3 Hz, Ar–H), 7.2 (3H, m, Ar–H), 6.4 (1H, t, 4.6 Hz, =CH), 5.65 (1H, br s, NH), 2.75 (2H, t, 7.9 Hz, CH_2), 2.3 (2H, m, =CHCH_2), 2.45 (9H, s, $C(CH_3)_3$); δ_C (100.6 MHz, $CDCl_3$) 168.2; 137.4; 136.1; 131.5; 129.9; 127.7; 127.6; 126.6; 124.9; 51.4; 28.8; 27.6; 22.8. IR (KBr ν (cm^{-1})) 3319 (NH), 1640 (CON); MS *m*/*z* (rel int.): 229 (63, M^+), 214 (7), 172 (38), 157 (95), 129 (100).

*4.6.3. 1-(N-Phenylcarboxamido)-3,4-dihydronaphthalene (**4b**).* Yield: 209 mg (84%); off-white solid, mp 173–174 °C; [found: C, 81.76; H, 6.21; N, 5.49; $C_{17}H_{15}NO$ requires C, 81.90; H, 6.06; N, 5.62%]; R_f ($CHCl_3$) 0.56; δ_H (400 MHz, $CDCl_3$) 7.7 (1H, br s, NH); 7.6 (2H, d, 7.8 Hz, Ph (*ortho*)); 7.45 (1H, d, 3.7 Hz, Ar–H); 7.32 (2H, t, 7.8 Hz, Ph (*meta*)); 7.2 (3H, m, Ar–H); 7.15 (2H, t, 7.3 Hz, Ph (*para*)); 6.6 (1H, t, 4.6 Hz, =CH); 2.8 (2H, t, 8.1 Hz, CH_2); 2.4 (2H, m, =CHCH_2). δ_C (100.6 MHz, $CDCl_3$) 166.8; 138.0; 136.7; 136.3; 132.3; 131.0; 129.0; 128.1; 128.0; 126.9; 125.1; 124.4; 120.0; 27.5; 23.0; IR (KBr ν (cm^{-1})) 3231 (NH); 1651 (CON); MS *m*/*z* (rel int.): 249 (80, M^+), 157 (100), 102 (7), 77 (11). MS (*m*/*z*/rel.int.): 249/80 (M^+), 77/11, 102/7, 157/100.

*4.6.4. 1-(N,N-(Pentan-1,5-diyl)carboxamido)-3,4-dihydronaphthalene (**4c**).* Yield: 217 mg (90%); white solid, mp 84–85 °C; [found: C, 79.54; H, 8.11; N, 5.60; $C_{16}H_{19}NO$ requires C, 79.63; H, 7.94; N, 5.80%]; R_f (10% EtOAc/$CHCl_3$) 0.69; δ_H (400 MHz, $CDCl_3$) 7.25–7.10 (3H, m, Ar–H); 7.05 (1H, d, 3.7 Hz, Ar–H); 6.05 (1H, t, 4.6 Hz, =CH); 3.7 (2H, br s, NCH_2); 3.25 (2H, br s, NCH_2); 2.8 (2H, t, 7.7 Hz, CH_2); 2.42–2.30 (2H, m, =CHCH_2); 1.6 (4H, br s, 2×CH_2); 1,4 (2H, br s, CH_2), δ_C (100.6 MHz, $CDCl_3$) 168.9; 136.1; 135.2; 131.4; 127.9; 127.7; 127.0; 126.7; 124.1; 48.1; 42.4; 27.4; 26.6; 25.7; 24.6; 22.7; IR (KBr ν (cm^{-1})) 1636 (CON); MS *m*/*z* (rel int.): 241 (100, M^+), 158 (43), 128 (84), 84 (22).

*4.6.5. 1-((N-Methoxycarbonylmethyl)carboxamido)-3,4-dihydronaphthalene (**4d**).* Yield: 223 mg (91%); off-white solid, mp 94–95 °C; [found: C, 68.40; H, 6.29; N, 5.55; $C_{14}H_{15}NO_3$ requires C, 68.56; H, 6.16; N, 5.71%]; R_f (30% EtOAc/$CHCl_3$) 0.70; δ_H (400 MHz, $CDCl_3$) 7.45 (1H, d, 7.4 Hz, Ar–H); 7.15 (3H, m, Ar–H); 6.5 (2H, br s, =CH+NH); 4.1 (2H, s, CH_2); 3.75 (3H, s, OCH_3); 2.75 (2H, t, 7.8 Hz, CH_2); 2.3 (2H, m, =CHCH_2). δ_C (100.6 MHz, $CDCl_3$) 170.4; 168.9; 136.1; 135.6; 132.1; 131.0; 127.8; 127.8; 126.7; 125.2; 52.3; 41.3; 27.5; 22.9. IR (KBr ν (cm^{-1})) 3321 (NH); 1752 (COO); 1656 (CON).

*4.6.6. 1-(N-(1-(Methoxycarbonyl)-ethyl)carboxamido)-3,4-dihydronaphthalene (**4e**).* Yield: 238 mg (92%); yellow solid, mp 89–90 °C; [found: C, 69.41; H, 6.69; N, 5.19; $C_{15}H_{17}NO_3$ requires C, 69.48; H, 6.61; N, 5.40%]; R_f (5% EtOAc/$CHCl_3$) 0.63; δ_H (400 MHz, $CDCl_3$) 7.45 (1H, d, 6.8 Hz, Ar–H); 7.18 (3H, m, Ar–H); 6.55 (1H, t, 4.7 Hz, =CH); 6.5 (1H, br s, NH); 4.72 (1H, quint, 7.3 Hz, *CH*CH_3); 3.75 (3H, s, OCH_3); 2.75 (2H, t, 7.7 Hz, CH_2); 2.3 (2H, m, =CHCH_2); 2.05 (3H, d, 7.3 Hz, CHCH_3). δ_C (100.6 MHz, $CDCl_3$) 173.5; 168.2; 136.1; 135.8; 131.9; 131.1; 127.8; 127.8, 126.7; 125.1; 52.4; 48.1; 27.5; 23.0; 18.3. IR (KBr ν (cm^{-1})) 3292 (NH); 1743 (COO); 1647 (CON). MS (*m*/*z*/rel.int.): 259 (28, M^+), 128 (55), 157 (100), 200 (14).

*4.6.7. 1-((N,N-1-Methoxycarbonylbutan-1,4-diyl)carboxamido)-3,4-dihydronaphthalene (**4f**, 3/1 mixture of two rotational isomers).* Yield: 251 mg (88%); yellow solid, mp 101–102 °C; [found: C, 71.40; H, 6.88; N, 4.79; $C_{17}H_{19}NO_3$ requires C, 71.56; H, 6.71; N, 4.91%]; R_f (20% EtOAc/$CHCl_3$) 0.56; δ_H (400 MHz, $CDCl_3$) 7.3 (1H, t, 7.4 Hz, Ar–H); 7.15–7.05 (3H, m, Ar–H); 6.2/6.05 (major/minor) (1H, t, 4.6 Hz, =CH); 4.6 (1H, m, NCH); 3.75 (3H, s, OCH_3); 3.4 (2H, m, NCH_2); 2.75 (2H, t, 8.1 Hz, CH_2); 2.35 (2H, m, =CHCH_2); 1.85–2.00 (4H, m, $(CH_2)_2$). d_C (100.6 MHz, $CDCl_3$) 172.9/172.7 (minor/major); 169.2/169.0 (minor/major); 136.4/136.3 (major/minor); 135.5/135.3 (minor/major); 130.9/130.5 (major/minor); 128.7/128.4 (major/minor); 127.83/127.72 (minor/major); 127.8/127.67 (minor/major); 126.9/126.7 (major/minor); 124.4/124.0 (major/minor); 60.5/58.4 (minor/major); 52.2/52.0 (major/minor); 48.6/46.0 (major/minor); 31.2/29.5 (minor/major); 27.4/27.1 (major/minor); 24.9/22.9 (major/minor); 22.7/22.5 (major/minor). IR (KBr ν (cm^{-1})) 1744 (COO); 1631 (CON). MS (*m*/*z*/rel.int.): 285 (28, M^+), 70 (16), 128 (56), 157 (100), 226 (28).

*4.6.8. 1-Methoxycarbonyl-3,4-dihydronaphthalene (**5**).* Yield: 147 mg (78%); highly viscous yellow material, [found: C, 76.50; H, 6.64; $C_{12}H_{12}O_2$ requires C, 76.57; H, 6.43%]; R_f (10% EtOAc/$CHCl_3$) 0.72; δ_H (400 MHz, $CDCl_3$) 7.8 (1H, d, 7.5 Hz, Ar–H); 7.12–7.28 (4H, m, Ar–H+=CH); 3.8 (3H, s, OCH_3); 2.75 (2H, t, 7.7 Hz, CH_2); 2.4 (2H, m, =CHCH_2). δ_C (100.6 MHz, $CDCl_3$) 167.0; 139.7; 136.2; 130.9; 130.8; 127.6; 127.5; 126.6; 126.0; 51.8; 27.5; 23.5. IR (KBr ν (cm^{-1})) 1720 (COO). MS (*m*/*z*/rel.int.): 188 (39, M^+), 129 (100), 157 (8).

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